

## **Towards a deeper understanding of coal-tar pitch structure and its relation to thermally induced pitch reactivity**

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Coal-tar pitch is the residue of the technical distillation of high-temperature coal-tar; it is obtained in 50 % yield, relative to crude coal-tar. Pitch serves predominantly as an important raw material for the manufacture of electrodes for electrochemical and electrothermal metallurgy (1). Moreover, it can be used for manufacturing pitch-based carbon fibres (2).

Since the appearance of the fundamental work of Brooks and Taylor (3) in 1965 of an intermediate mesophase state in the carbonization of pitches interest in pitch research has grown tremendously. It became also increasingly evident that a deeper understanding of the structure and the thermally induced (carbonization) chemistry of coal-tar pitch is of high interest from both the industrial and scientific point of view.

### **1. The toluene-soluble fraction of coal-tar pitch / molecular weight range and chemical structure principles**

The toluene-soluble fraction ("TS-fraction") of pitch typically amounts to ca. 75 % per weight, relative to the entire pitch.

As follows from gas chromatography/mass spectrometry examination the smallest molecules present in the TS-fraction (in very low concentrations) have molecular weights of about 200 Dalton. Typical examples are: fluorene, phenanthrene, anthracene, carbazole, pyrene and fluoranthene. However, molecular mass of TS-fraction constituents cover a wide range; for example, TS-subfractions with mean molecular masses up to approximately 2200 Dalton have been isolated by a chemical method (Charge-Transfer Fractionation, see below). <sup>1</sup>H nmr spectroscopy revealed that these fractions are highly aromatic in nature. This leads to an important and interesting question: Are the higher-molecular TS-fraction constituents large monomeric polycyclic systems or rather oligomeric systems where medium-sized aromatic units are connected by e.g. C-C single bonds (oligo-aryl type), -CH<sub>2</sub>-groups, ether bridges, etc.? The two possible structure models of the higher molecular TS-fraction constituents are schematically depicted in Fig.1. The circles symbolize aromatic units of different size, the lines C-C single bonds between aromatic units and -X- denotes bridging functions.

Experimental findings obtained with the higher-molecular weight TS-subfractions indicate that the oligomeric structure model is much more likely:

- Solubility in organic solvents: In spite of their high molecular weights, the materials are surprisingly readily soluble in organic solvents. The non-planar (twisted) arrangement of the aryl/heteroaryl units, due to steric hindrance, explains in known fashion the relatively good solubility of the oligomeric systems.
- Clathration ability with respect to smaller aromatic molecules: It has been observed that the higher-molecular TS-subfractions contain smaller molecules e.g., fluoranthene, pyrene, benzopyrenes, and others which in spite of their good solubility in organic solvents cannot easily be removed by extraction with e.g., toluene at boiling temperature (4). It must therefore be concluded that these smaller "guest" molecules are relatively strongly bonded to the higher-molecular

components which act as "host" molecules. Again an oligomeric structure model of the host molecules provides a much more obvious explanation of their clathration ability than a monomeric structure model can do. For an oligomeric structure it can be assumed that it contains three-dimensional "cages" which can act as traps captivating the smaller guest molecules.

- nmr spectroscopy: As discussed elsewhere (5, 6)  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra also support strongly the oligomeric structure model.

## 2. The basic character of the higher-molecular portion of the TS-fraction

Assuming a statistical distribution of nitrogen among pitch constituents it has to be concluded that the probability for finding a nitrogen containing molecule in a pitch fraction increases with increasing molecular mass of the fraction. On this assumption and in spite of the rather low nitrogen content (typically 1 %) of the TS-fraction, the higher-molecular portion of the TS-fraction may be expected to contain a relatively large amount of nitrogen-containing compounds. By treatment of a toluene solution of coal-tar pitch with gaseous HCl (at room or boiling temperature) a precipitate of hydrochlorides of organic bases is obtained in 27 % yield, relative to TS-fraction (26 % calc. for the Cl-free fraction). It has been shown by model experiments that under the experimental conditions used only basic nitrogen-containing compounds form insoluble hydrochlorides while polycyclic aromatic hydrocarbons, carbazoles, and oxygen containing compounds do not (4). As found by GC/MS approximately 90 % of the basic TS-subfraction consists of molecules with molecular weight  $> 300$  Dalton. The higher-molecular mass portion of the basic TS-subfraction shows the properties of an oligomeric system as described in section 1. With regard to a further specification of our model of the higher-molecular portion of the TS-fraction we can now conclude that most of the oligomeric molecules contain at least 1 basic nitrogen atom. Besides that other N functions (carbazole structures) as well as O and S containing functions are present as follows from elemental analyses.

The basic TS-subfraction can be further separated by a chemical method that has been termed "Charge-Transfer Fractionation" (CTF) (4,5,6). The first step in the CTF of pitches or pitch fractions is to prepare a solution in a suitable solvent; the solvents most widely used in CTF are toluene and chloroform. An electron acceptor species (picric acid or elementary iodine) is then added to the solution at room temperature. Immediately after the acceptor has been added a mixture of charge-transfer complexes of pitch constituents precipitates from the solution and is isolated by filtration. It has been shown that the nitrogen-containing basic pitch constituents are the compounds that predominantly form CT complexes (4). Decomposition of the CT complexes allows the recovery of the uncomplexed (electron donor) pitch molecules. The most important experimental parameter in the CTF of pitches is R, the ratio per weight of electron acceptor to pitch (or pitch fraction) dissolved (7). With decreasing R the yield of CT complexes obtained decreases. The same applies to the amount of electron acceptor present in the complexes. The nitrogen content of the uncomplexed donor material (obtained after decomposition of the complexes) also decreases with decreasing R while the mean molecular mass of the material increases. Clearly CTF fractionates the basic TS-constituents according to molecular mass. An example of the relation between R and the mean molecular mass of basic TS-subfractions obtained by CTF (electron acceptor: picric acid) is given in Fig.2a. Similarly Fig.2b shows the relation between R and the nitrogen content of the fractions obtained, while Fig.2c gives the relation between mean molecular mass and nitrogen content of these fractions.

### 3. Do pitches contain very large monomeric polycyclic aromatics ?

The idea that the higher-molecular portion of the TS-fraction consists predominantly of oligomeric systems where medium-sized aromatic/heteroaromatic units are connected by C-C single bonds and bridging functions, does, of course, not exclude the possibility that pitches also contain very large monomeric polycyclic aromatic systems.

The presence of such systems may be particularly suspected in those pitch fractions that are only sparingly soluble in organic solvents. This applies to e.g., the toluene and the chloroform insoluble fractions. Electrical measurements, in fact, indicate that these fractions rather consist of very large monomeric aromatics than of oligomeric systems.

It is well established that polycyclic aromatic hydrocarbons, after addition of small amounts of iodine, are electrical semiconductors. Fig.3a shows the exponential dependence of the electrical resistance on molecular size for the polyacenes (after addition of 1 % iodine). Electrical resistance decreases with increasing molecular size. For theoretical reasons this must apply to all topologies. In Fig.3b the yield of chloroform-insoluble material of various coal-tar pitches is plotted against the logarithm of the electrical resistance (measured after addition of 1 % iodine) of the chloroform-insoluble fractions. An exponential decrease of electrical resistance with increasing yield of chloroform-insoluble material is observed (8). The preliminary though most likely interpretation of this result includes the assumptions that (i) the yield of the chloroform-insoluble fraction increases with increasing mean molecular weight of the fraction and (ii) (by analogy with the result obtained for the acenes) the size of the fully-conjugated aromatic systems present increases regularly with molecular weight. To fit the latter assumption with the oligomeric structure model additional assumptions on the structure of the systems would be necessary.

### 4. Carbonization chemistry of medium-sized polycyclic aromatic pitch constituents

The reaction types characteristic of the thermal chemistry of medium-sized pitch constituents were examined taking by way of example perylene (I) (Fig.4) as the model substance (9). The thermolysis experiments were carried out in isothermal conditions at 450°C in an argon atmosphere. After a reaction time of 20 h perylene conversion amounted to 42 %. The compounds identified from the liquid phase thermolysis of perylene are shown in Fig.4. The yield of products formed by condensation through loss of hydrogen ("aromatic growth"), i.e., biaryls IV, V, and VI, higher-molecular peri-condensed systems II and III and semicoke-like material was found to amount to 85 % in total, related to converted starting material. In addition fragmentation products (compounds VII - X) were formed in approximately 5 % yield. Formation of fragmentation products occurs by hydrogen transfer to intact perylene molecules and subsequent splitting of C-C single bonds initially formed. Due to fragmentation reactions methyl and ethyl hydrocarbon radicals are also formed that lead to alkylated products (compounds XI - XV) of the parent hydrocarbon.

Whereas in terms of quality the thermal chemistry of polycyclic aromatic hydrocarbons and structurally related heterocyclic systems is extensively independent of the structure of the reactants, in terms of quantity a heavy reactant depend-

ence is evident, i.e., in thermolytic reactions the conversion rate of hydrocarbons and heterocycles varies greatly with their size and topology. Carbonization rates of the polycyclic aromatic hydrocarbons listed in Fig.5 have been measured (10). Highly purified samples of each hydrocarbon were isothermally treated in sealed glass tubes at 430°C, i.e., above the melting points of the compounds, for 4 h. The conversion rates were determined by uv/vis spectroscopy and high-pressure liquid chromatography. Dependent on size and topology of the systems conversion rates range from 9 to 99 %, related to starting material. A linear free energy relation between the logarithms of conversion rates and a reactivity index (lowest Dewar localization energy) derived from MO theory has also been observed (10).

#### 5. Carbonization chemistry of coal-tar pitch fractions/role of mean molecular weight, structure and nitrogen content

Carbonization experiments in liquid phase (430°C) clearly revealed that the higher-molecular basic TS-subfraction obtained with gaseous HCl (see section 2) is much more reactive than the corresponding lower-molecular non-basic material obtained from the mother liquor of HCl treatment. Similarly TS-subfractions obtained by CTF (section 2) are more reactive than the TS-fraction itself or the entire pitch. This follows unambiguously from formation rates of toluene-insoluble material (TI), relative rates of mesophase formation as well as from activation energies of TI and QI formation (QI = quinoline insoluble material). For example, activation energy of QI formation from the entire pitch amounts to 36 kcal/mol but to 17 kcal/mol from a CT fraction obtained with picric acid as the electron acceptor ( $R = 0.05$ , see section 2) (6, 11).

The thermally more reactive materials are distinguished from the less reactive ones by: (1) higher mean molecular weight, (2) probably an oligomeric structure (as opposed to the assumed monomeric structure of the less reactive material) and (3) by slightly higher nitrogen contents.

For all topologies of polycyclic aromatic systems reactivity increases with molecular size. Therefore an increase of thermal reactivity of pitch fractions with mean molecular weight is not unexpected. An oligomeric structure of the reacting material is particularly suited for intramolecular cyclization reactions. The drastic reduction in solubility following thermal treatment of the reactive pitch fractions can be easily explained with the formation of large planar aromatic systems. As is known from numerous examples planar aromatic compounds are much less soluble in organic solvents compared to non-planar ones with the same molecular size. There is some experimental evidence (7, 12) that nitrogen containing constituents enhance the thermal reactivity of pitch fractions. The effect, however, has been shown to be rather small (13). It cannot quantitatively explain the pronounced thermal reactivity of pitch fractions obtained by e.g., CTF (14).

In summary, the higher thermal reactivity of pitch fractions obtained by CTF or by treatment of the TS-fraction with gaseous HCl compared to that of the entire TS-material can be explained with the higher molecular weights of these fractions and particularly with their proposed oligomeric structure.

## 6. Role of free radicals and their precursor molecules in pitch carbonization

Although it is controversial whether free radicals play a dominant role in the **primary** step of the thermally induced polymerization of polycyclic aromatic hydrocarbons (15, 16), the importance of free radical formation in pitch carbonization has been unambiguously proven (17). Because of their much longer lifetimes  $\pi$ -radicals are more relevant than  $\sigma$ -radicals (15). The most important  $\pi$ -radical precursor molecules present in pitch are dihydro aromatics of the 9,10-dihydro-anthracene type, amines, and phenols. The  $\pi$ -radicals are formed by thermally induced cleavage of the CH, OH, and NH bonds, respectively. Thermally abstractable hydrogen from CH<sub>2</sub>, OH and NH groups amounts in total to approximately  $6 \cdot 10^{-2}$  % H, relative to the entire pitch (6).

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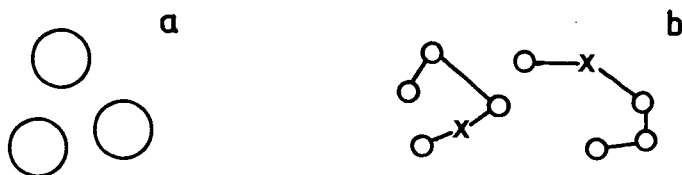


Fig.1. Structure models of higher-molecular TS-fraction constituents: a) "monomeric", b) "oligomeric" model.

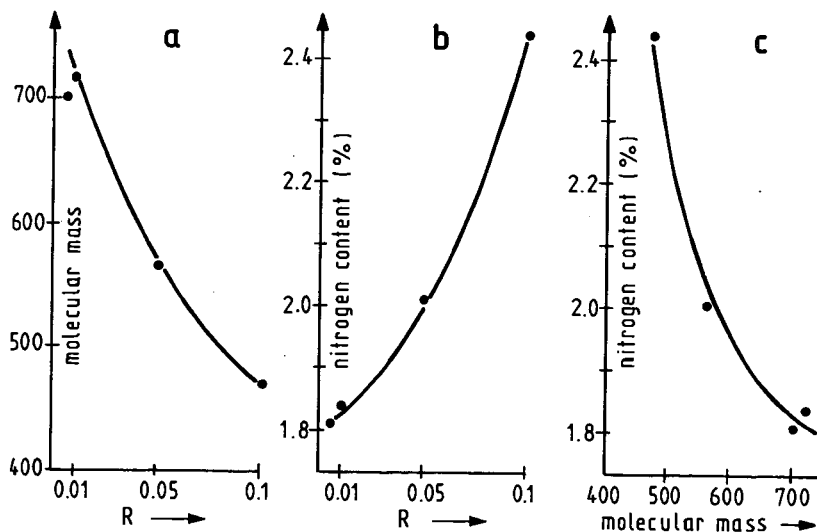


Fig.2. Charge-Transfer-Fractionation. - Relation between ratio R (per weight) of picric acid: pitch dissolved and molecular mass (a) or nitrogen content (b) of CT fractions obtained; (c) relation between molecular mass and nitrogen content of CT fractions.

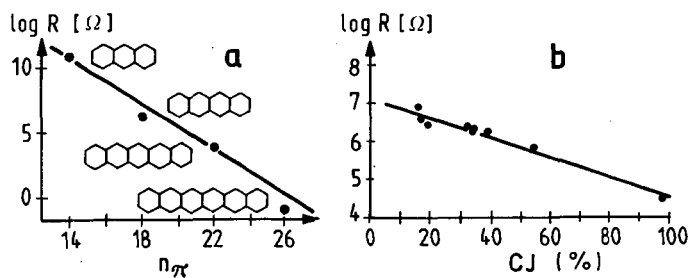


Fig. 3. (a) Relation between electrical resistance R (after addition of 1 % iodine) and number of  $\pi$ -electrons of the polyacenes; (b) relation between R and yield of the chloroform-insoluble fraction of 9 coal-tar pitches.

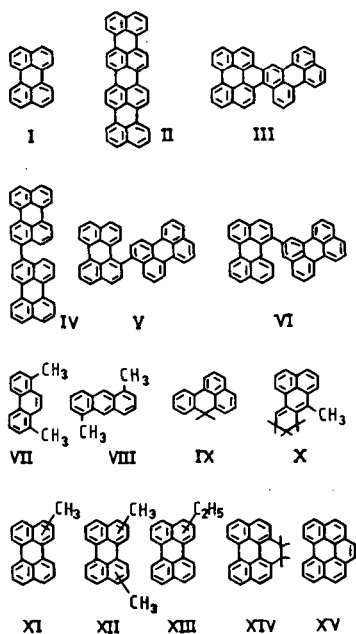


Fig. 4. Identified compounds from the thermolysis (450°C) of perylene.


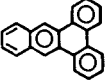
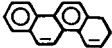

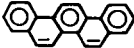
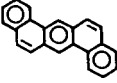

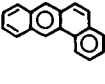

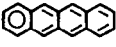
Hydrocarbon	Conversion rate (%)	Hydrocarbon	Conversion rate (%)
	9		36
	20		40
	24		50
	27		53
	30		99

Fig.5. Carbonization rates (430°C, 4 h) of polycyclic aromatic hydrocarbons